REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
20-11-2012	Final Report	20-Nov-2009 - 31-Dec-2010

4. TITLE AND SUBTITLE
Conversion of Small Algal Oil Sample to JP-8

5a. CONTRACT NUMBER

5b. GRANT NUMBER
W911NF-10-C-0021

5c. PROGRAM ELEMENT NUMBER
9620BB

6. AUTHORS
F. S. Lupton

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
UOP LLC
25 East Algonquin

Des Plaines, IL 60017 -

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
57239-CH-DRP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
A small sample of Algal oil was received by UOP for conversion to synthetic paraffinic kerosene (SPK) for blending with HiSol-10 aromatics to produce a sample of JP-8 avaiation turbine fuel. As received this sample was not acceptable for conversion to SPK and was sent to POS for pre-treatment. A small sample of oil, approximately 720 ml was sent to UOP for processing into SPK. This sample was processed using the UOP Green Jet process to make an SPK product. The SPK was blended with HiSol-10 at a level of 75% SPK and 24% HiSol-10 to produce

15. SUBJECT TERMS
Algal Oil, JP-8, SPK, MIL-DTL-83133G

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Steve Lupton
UU	UU	UU	UU		19b. TELEPHONE NUMBER
					847-391-3224

Report Title

Conversion of Small Algal Oil Sample to JP-8

ABSTRACT

A small sample of Algal oil was received by UOP for conversion to synthetic paraffinic kerosene (SPK) for blending with HiSol-10 aromatics to produce a sample of JP-8 avaiation turbine fuel. As received this sample was not acceptable for conversion to SPK and was sent to POS for pre-treatment. A small sample of oil, approximately 720 ml was sent to UOP for processing into SPK. This sample was processed using the UOP Green Jet process to make an SPK product. The SPK was blended with HiSol-10 at a level of 75% SPK and 24% HiSol-10 to produce 300 ml of final JP-8 fuel. This sample was forwarded to the Fuels Branch of the Air Force Research Lab at Wright-Patterson Air Force Base for analysis. This sample met all specifications of Mil Spec MIL-DTL-83133G for MP-8 aviation turbine fuel.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: .....

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): .....

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: .....

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense .....

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: .....

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attached.

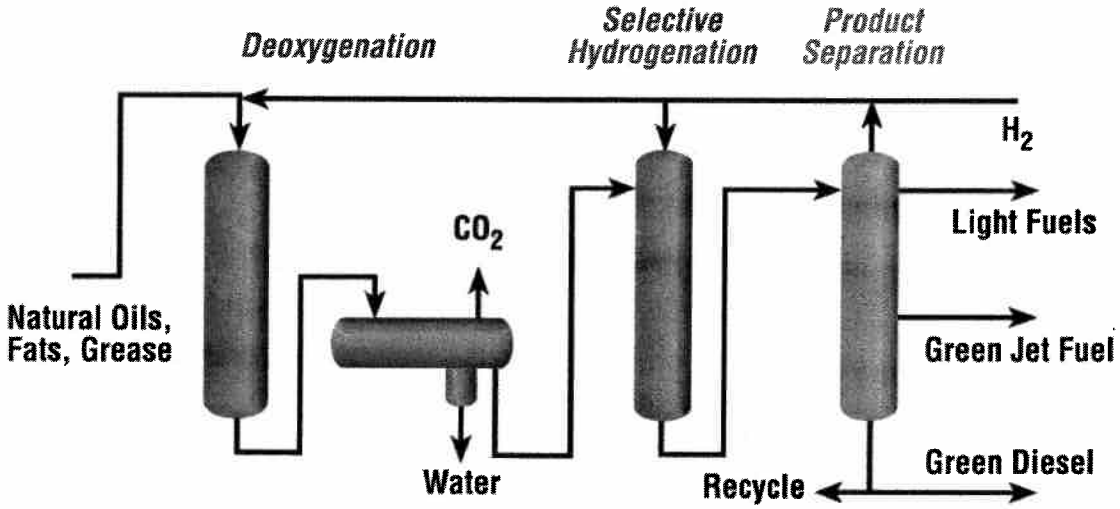
Technology Transfer

DARPA Project W911NF-10-C-0021

Conversion of Small Algal Oil Sample to JP-8

Statement of the Problem Studied: The Objective of this project was to convert a small sample of Algal oil into Synthetic Paraffinic Kerosene (SPK) to be blended with a petroleum derived aromatics (HiSol 10) to create a bio-fuel equivalent to JP-8 aviation turbine fuel. The original concept was to process 1-gallon of DARPA supplied Algal oil into SPK and produce as large a volume of blended SPK blended with HiSol as possible to maximize the volume of final JP-8 product for testing by the Fuels & Energy Branch of the US Air Force Research Laboratory (RZPF).

Background: as part of the previous DARPA Funded project, W911NF-07-C-0049: Feed-Flexible Processing of Oil-Rich Crops to JP-8, UOP developed a process for the conversion of triglyceride oils derived from oil crops into synthetic paraffinic kerosene (SPK) that can be blended with petroleum derived aromatics to produce JP-8 jet fuel. This process has been commercialized by UOP as the "Green Jet" process and is illustrated in the following figure:



The process involves three steps:

1. The first step involves deoxygenation and saturation of the carbon double bonds in the fatty acid molecules comprising the triglyceride oil which creates straight chain n-alkanes and propane

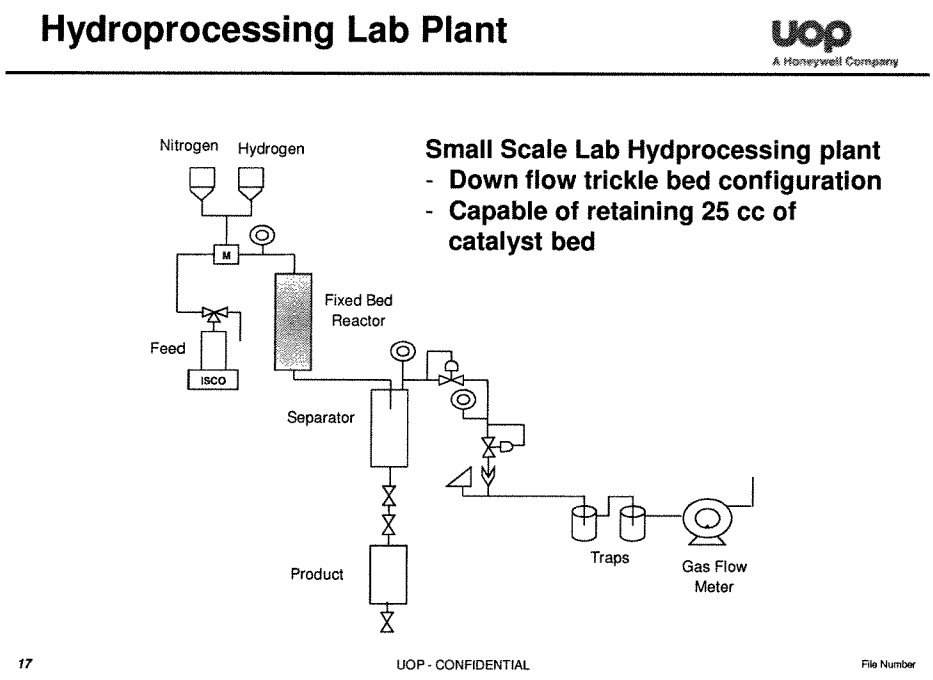
2. The second step involves isomerization and cracking of the n-alkanes (predominately carbon number C15 – C18) into smaller molecular weight branched iso-alkanes (predominately carbon number C6 – C14)

3. The third step involves fractionation of the isomerized and cracked iso-alkane fraction into a naphtha cut (approx. initial boiling point to 150°C) and a Jet cut (approx 150°C to 260°C).

The SPK Jet cut is then blended with HiSol 10 at a volumetric basis of 24% HiSol 10 with 76% SPK to produce a JP-8 sample that meets the criteria of <25% aromatic content by volume.

For the small DARPA project this conversion was to be done in bench scale Lab plants at UOP's Des Plaines Research Center. A single plant was used for both deoxygenation and also the isomerization/cracking step. The catalyst in the plant was changed out between the deoxygenation step and the isom/cracking step. A commercial hydrotreating catalyst was used for the deoxygenation step whereas a specific isomerization/cracking catalyst developed under DARPA project W911NF-07-C-0049 was used for the isomerization/cracking step. A schematic of the Lab Scale Hydroprocessing Plant is shown in figure 1:

Figure 1: Configuration of lab Scale Hydroprocessing Plant for Deoxygenation and Isomerization/cracking of Algal Oil to SPK



The catalytic deoxygenation stage of the process removes all the oxygen and saturates the double bonds of both triglycerides and free fatty acid feeds. Oxygen is completely removed through competing mechanisms: decarboxylation (DeCOx) and hydrodeoxygenation (HDO). One carbon is removed and lost in the DeCOx reaction producing COx and a paraffin chain with an odd number of carbon atoms. One mole of hydrogen is required in the hydrodeoxygenation pathway to produce water and a long-chain paraffin with the same even number of carbons as found in the fatty acid chain of the feed. Note that since decarboxylation removes a carbon from the fatty acid chain the final yield of paraffins will be lower than paraffins produced through hydrodeoxygenation.

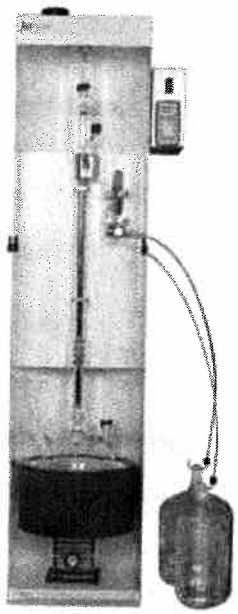
The hydrogenation of all double bonds occurs independently of the deoxygenation mechanism to produce a hydrogen-saturated paraffin product. This erases one of the key

differentiators of natural oils; location and number of double bonds in the fatty acid chains. The final paraffin product has a carbon-number composition very similar to the fatty acid carbon number distribution of the starting oil.

The deoxygenation product contains mostly n-paraffins in the C15-C18 carbon range. These high molecular weight molecules do not have properties to meet jet fuel specification such as freeze point. A selective cracking step is required to reduce the carbon number from C15-C18 to the jet fuel range from ~C9-C15. This step is called selective cracking because over cracking will result in low yields to jet range paraffins and high yields of light ends (C1-C4) and naphtha (C5-C8), both outside the jet fuel range. These products of over cracking have much lower economic value than diesel or jet range paraffins. Isomerization is also required to lower the freeze point.

Fractionation of the deoxygenated and isomerized/cracked algal oil was conducted in a B/R Instruments B/R I9600 High Efficiency Distillation System similar to the one shown in Figure 2:

Figure 2: B/R Instrument 9600 High Efficiency Distillation System



The process conditions used for conversion of algal oil to SPK were the same as those used for the conversion of vegetable oil to SPK as outlined in the final report for project W911NF-07-C-0049: Feed-Flexible Processing of Oil-Rich Crops to JP-8

Summary of the Most Important Results: the algal "oil" as received from DARPA was not an oil but rather a slurry of concentrated algal biomass, referred to as a "green goo". Microscopic evaluation indicated that the oil appeared to be predominately intact algal cells. After discussion with DARPA, the algal sample was shipped to POS Pilot Plants Inc. in Saskatoon, Canada for oil extraction.

The oil was processed at POS using a proprietary process developed by POS for oil extraction from Algae the sample was forwarded to EERC for splitting between different project participants for processing to fuels.

UOP received approximately 720 g of extracted oil from the EERC split of the POS extracted material. The material received was not like previous samples of triglyceride oil processed by UOP. The oil was very dark and very viscous as can be seen in the following Figure:

Figure 3: Oil Received from POS

The oil did not flow freely until it was heated to a temperature of at least 45°C – 50°C Based upon these physical properties and appearance it looked as if this sample contained a significant amount of impurities. An elemental analysis of the oil was performed.

The results of this analysis of the oil received from POS are shown in table 1. The level of nitrogen appears high in this sample and the oxygen appears lower than for typical algal oils. The high nitrogen and high magnesium in this sample along with very dark green color is an indication that the oil is heavily contaminated with chlorophyll and other algal pigments. The relatively high acid number (>50 mg KOH/g) indicated a high proportion of free fatty acids. The oil also had high chloride content which combined with the samples acidity, is a challenge to reactor metallurgy.

None the less, an attempt was made to convert this sample to SPK in a small UOP lab plant.

Table 1: Analysis of Algal oil received

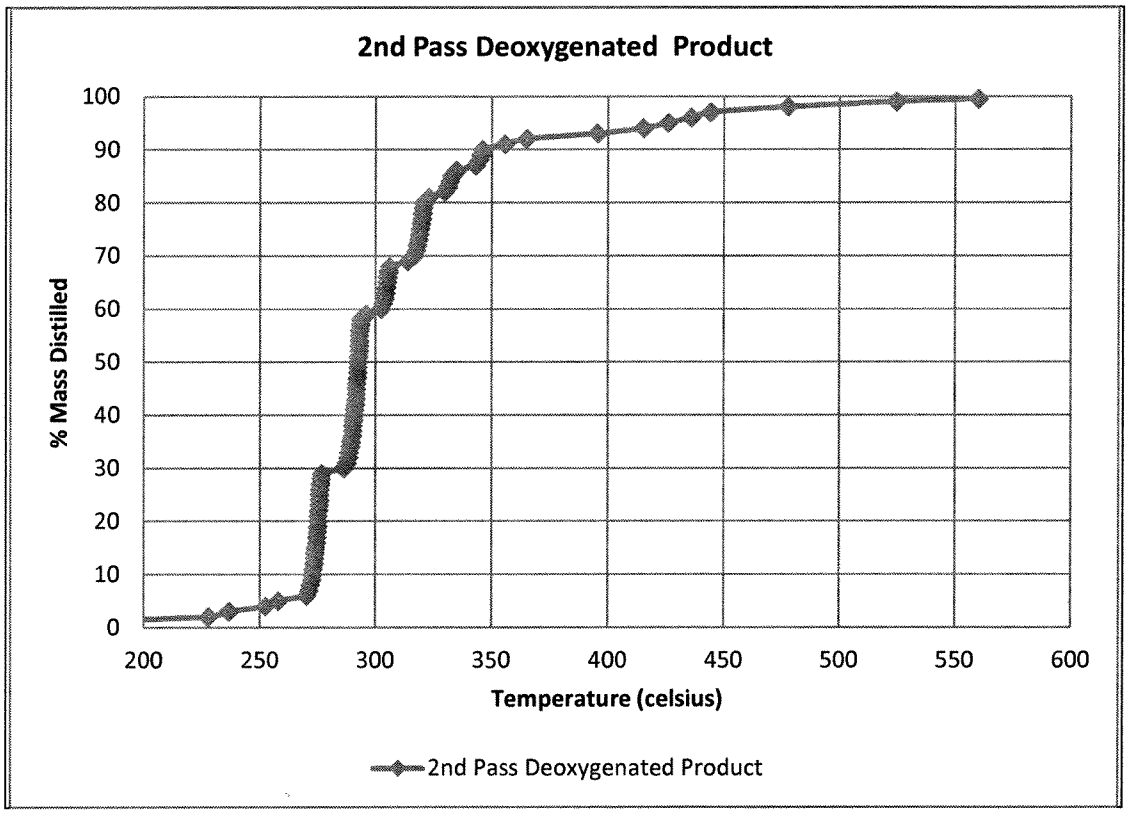
Carbon	79.9	mass%
Hydrogen	11.3	mass%
Nitrogen	1.13	mass%
Oxygen	7.67	mass%
Sulfur	74	ppm
Chloride	137	ppm
Metals		
Al	0.18	ppm
Ca	19.5	ppm
Co	< 0.08	ppm
Cr	< 0.08	ppm
Cu	0.87	ppm
Fe	2.43	ppm
Mg	201	ppm
Mn	0.77	ppm
Mo	0.16	ppm
Na	13.5	ppm
Ni	< 0.08	ppm
P	113	ppm
Pb	< 0.2	ppm
Sn	< 0.2	ppm
Sr	3.97	ppm
Ti	< 0.08	ppm
V	< 0.08	ppm
Zn	2.07	ppm
K	2.9	ppm
Acid Number	51.7	mg KOH per g

Deoxygenation of Algal Oil: Algal oil was processed in the lab plant under deoxygenation conditions with a commercial hydrotreating catalyst. At the initial processing conditions, the sample still appeared to be quite dark. Analysis of oxygen in the product at this condition gave an oxygen level of 1.24% in the product. As a result the processing temperature was increased by 20°C. This resulted in the oxygen level in the final product dropping to 0.25%, much lower but still too high. As a result, the product was re-processed in a second pass through the deoxygenation reactor to reduce oxygen to <0.04%.

Nitrogen was reduced from 1.13% in the first pass deoxygenation to 0.43% and was further reduced to 0.14% after the second pass.

The simulated distillation of the deoxygenated product indicated that the material had a heavy tail of larger molecular weight material as shown in Figure 4:

Figure 4: Simulated Distillation of 2nd Pass Deoxygenated Product



Isomerization/Cracking of the Deoxygenated Algal Oil: The presence of the heavy tail indicated that two cracking and isomerization steps would be needed to maximize the amount of material in the jet range. A heavy fraction (350C+) was recovered by spinning band distillation after the first isomerization /cracking and fractionation step. This material was reprocessed in the isomerization/cracking step a second time. This avoided the over cracking of that material that was already in the jet range to Naphtha during a second pass and only heavy material was reprocessed. After the reprocessed material was blended back with the original isomerized/cracked material it was re-fractionated by spinning band into naphtha, jet and diesel cuts. The jet cut that was selected in this fractionation was 145°C to 270°C.

This fraction was analyzed and found to have the following density, flash point and freeze point characteristics:

Specification Test	MIL-DTL-83133G Spec Requirement	Result
Density @ 15°C, kg/L	0.775 - 0.840	0.7669
Flash point, °C	≥38	56.5
Freeze Point, °C	≤-47	-36.9

The density of this cut is lower than the MIL-DTL-83133G Spec Requirement but this will be compensated by addition of HiSol aromatics but the freeze point was considerably higher than the MIL-DTL-83133G Specification. Therefore it was decided to re-blend the naphtha and jet material and re-fractionate a jet cut between 140°C – 270°C.

This cut had flash and freeze properties that met the MIL-DTL-83133G specifications:

Specification Test	MIL-DTL-83133G Spec Requirement	Result
Density @ 15°C, kg/L	0.775 - 0.840	0.7618
Flash point, °C	≥38	48.4
Freeze Point, °C	≤-47	-59.1

The maximum allowable aromatic content of JP-8 is 25 vol%. In order to maximize the amount of JP-8 sample from the algal SPK, aromatics were added to give a final aromatic content of 24 vol%. This sample was shipped to the Fuels & Energy Branch of the US Air Force Research Laboratory (RZPF) for analysis with respect to the MIL-DTL-83133G Spec Requirements.

AFRL /RZPF reported the following analysis of the fuel. The fuel was evaluated according to the Tier I of RZPF's "Alternative and Experimental Jet Fuel and Jet Fuel Blend Stock Evaluation." Comparisons were made to a representative petroleum-derived JP-8 jet fuel, and the current JP-8 specification (Military Specification MIL-DTL-83133G).

All the considered fuel properties satisfied current requirements as shown in the following figures & Tables:

Table 1. List of Fuel Samples Used in this Study

POSF No.	Manufacturer/ Source	Fuel Description
7051	EERC-UOP	Algal Jet Fuel-100920
4751	WPAFB	JP-8

Table 2. Results of Specification Testing

Specification Test	MIL-DTL-83133G Spec Requirement	7051 Algal Jet Fuel 100920	4751 JP-8
Aromatics, vol %	≤25	24.3	18.8
Olefins, vol %	≤5	0.8	0.8
Heat of Combustion (measured), MJ/Kg	≥42.8	43.2	43.3
Distillation:			
IBP, °C		159	159
10% recovered, °C	≤205	173	182
20% recovered, °C		178	189
50% recovered, °C		192	208
90% recovered, °C		244	244
EP, °C	≤300	256	265
Residue, % vol	≤1.5	1.0	1.3
Loss, % vol	≤1.5	NA	0.8
Flash point, °C	≥38	46	51
Freeze Point, °C	≤-47	-62	-50
API Gravity @ 60°F	37.0 - 51.0	47.8	44.4
Density @ 15°C, kg/L	0.775 - 0.840	0.789	0.804

Table 3. Aromatic Species Analysis by D6379 for Biofuels and JP-8 Fuel

	7051 Algal Jet Fuel 100920	4751 JP-8
D6379 (volume %)		
Mono-aromatics	24.0	17.5
Di-aromatics	<0.1	1.2
Total Aromatics	**24.0**	**18.7**
Total Saturates	**76.0**	**81.3**

Table 3. Hydrocarbon Type Analysis by D2425 for Biofuels and JP-8 Fuel

	7051 Algal Jet Fuel 100920	4751 JP-8
D2425 (mass %)		
Paraffins (normal + iso)	69	49
Cycloparaffins	5	30
Alkylbenzenes	25	13
Indans and Tetralins	0.7	5.8
Indenes and C_nH_{2n-10}	<0.3	0.6
Naphthalene	<0.3	<0.3
Naphthalenes	<0.3	1.0
Acenaphthenes	<0.3	<0.3
Acenaphthylenes	<0.3	<0.3
Tricyclic Aromatics	<0.3	<0.3
Total	100	100

Table 4. Weight Percent of n-Paraffins for Biofuels and JP-8 Fuel

	7051 Algal Jet Fuel 100920	4751 JP-8
n-Paraffins (weight %)		
n-Heptane	0.01	0.10
n-Octane	0.04	0.34
n-Nonane	1.18	1.21
n-Decane	1.60	3.48
n-Undecane	1.29	4.24
n-Dodecane	0.93	3.71
n-Tridecane	0.75	2.84
n-Tetradecane	0.42	1.79
n-Pentadecane	0.52	0.87
n-Hexadecane	0.10	0.27
n-Heptadecane	0.002	0.089
n-Octadecane	<0.001	0.024
n-Nonadecane	<0.001	0.008
Total n-Paraffins	**6.8**	**19.0**

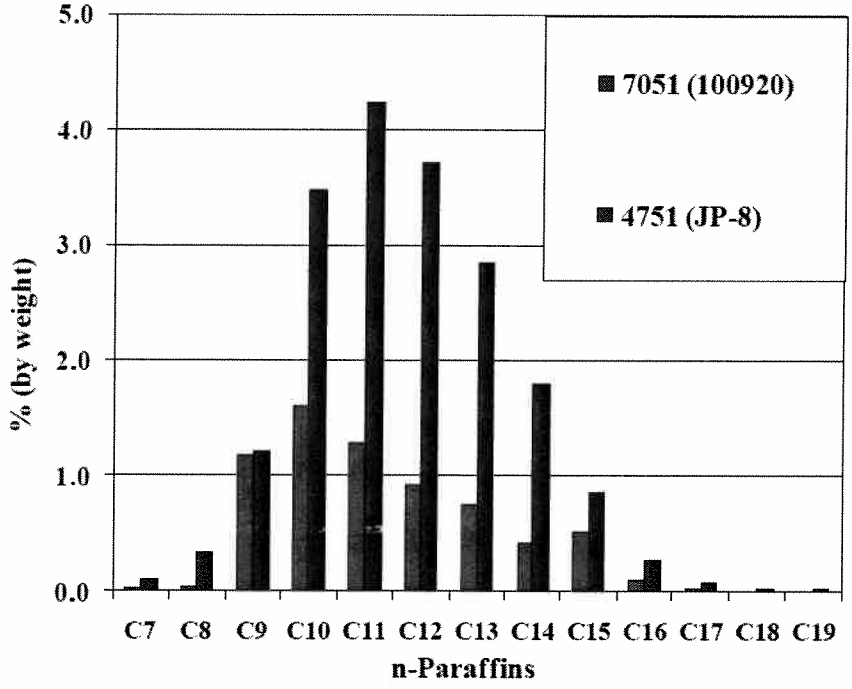


Figure 1. Weight Percent of n-Paraffins (C7-C19) for Biofuels and JP-8

Weight % n-Paraffins				
	C_7-C_9	C_{10}-C_{13}	C_{14}-C_{16}	C_{17}-C_{19}
7051	1.2	4.6	1.0	0.002
4751	1.7	14.3	2.9	0.12

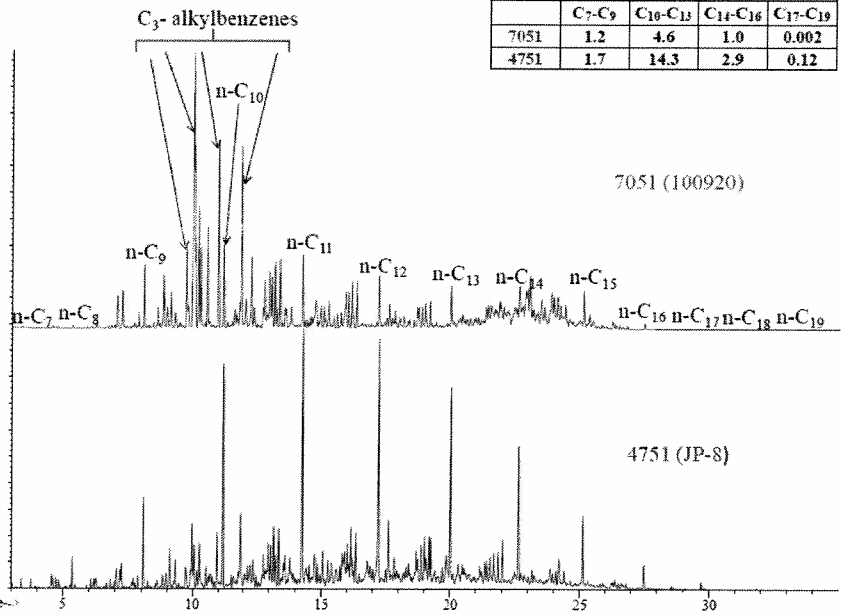


Figure 2. Chromatograms of Biofuels and JP-8 Fuel

Table 6. Data from QCM Thermal Stability Analysis

POSF No.	Fuel Description	15 Hr Mass Accumulation ($\mu g/cm^2$)
7051	Algal Jet Fuel - 100920	1.9
4751	JP-8	3.0

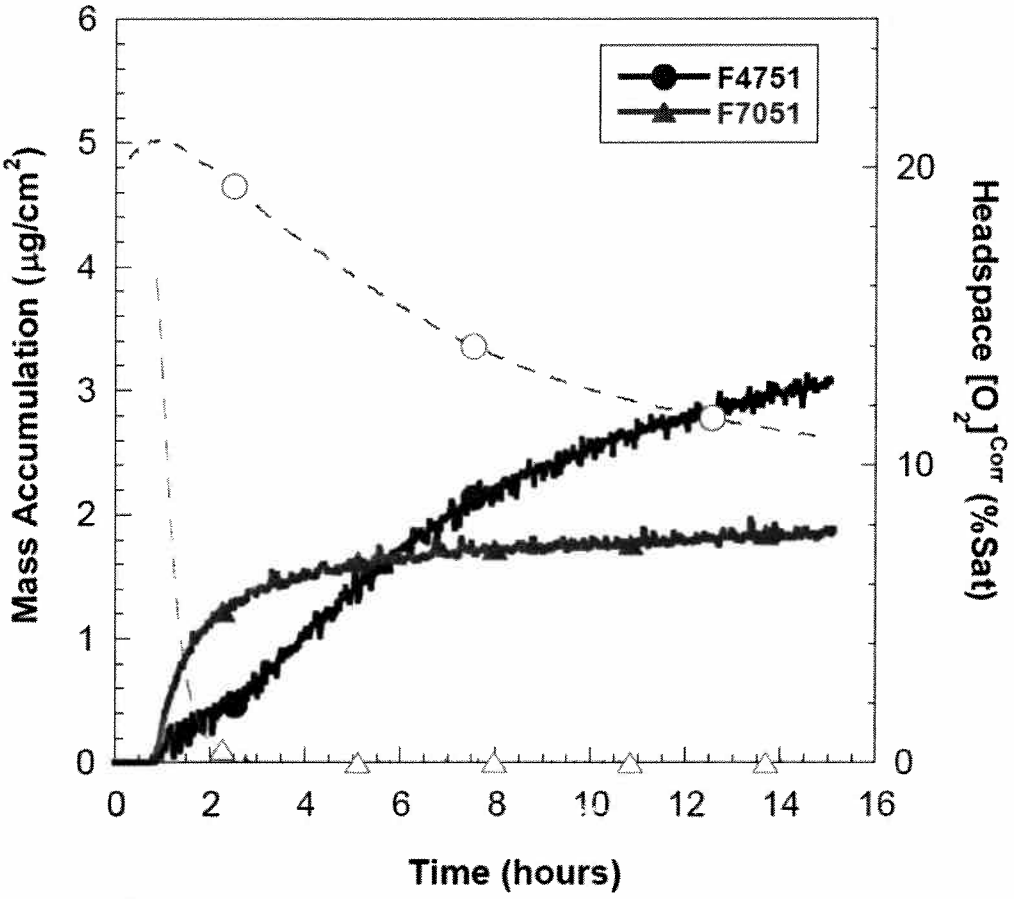


Figure 3. Mass Accumulation (solid curves, closed markers) and Headspace Oxygen Profiles (dashed curves, open markers) form QCM Analysis of Biofuels and JP-8 Fuel